



Highly reproducible and photocurrent hysteresis-less planar perovskite solar cells with a modified solvent annealing method

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ABSTRACT

Highly reproducible and photocurrent hysteresis-less inverted planar perovskite solar cells were demonstrated by a modified solvent annealing method in a two-step solution deposition (modified method). Pbl₂ film was annealing at 40 °C using the residue solvent after spin-coating, which facilitated the subsequent CH₃NH₃Pbl₃ perovskite active layer with high photovoltaic properties. The resulting device present a power conversion efficiency of 12.12%, which increased 42.7% compared with that of the control device fabricated as literatures.

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1. Introduction

Only in the past few years, solution-processed inorganic-organic metal hybrid perovskite have been used in solar cell, the resulting perovskite solar cells (PVSCs) are identified as star products in the third-generation solar cells and most promising as good as today's commercial champions—silicon based solar cells. To date, various modified methods focused on one-step solution deposition (one-step procedure) have been investigated, which include solvent engineering (N.J. Jeon et al., 2014), compositional engineering (Jeon et al., 2015), interface engineering (Zhou et al., 2014), thermal annealing (Hsu et al., 2014), solvent annealing (You et al., 2014b) and additives (Mei et al., 2014) in meso-superstructured, solid state mesoscopic, and planar PVSCs. The power conversion efficiency (PCE) over 20% has been achieved with TiO₂ as an electron transport layer (ETL) (Yang et al., 2015). Meanwhile, there are also growing interests in the inverted planar structures typically using PCBM as ETL because of the simple fabrication process (Heo et al., 2015; Nie et al., 2015). PCEs of the inverted planar PVSCs was lower than those of normal planar PVSCs, which cast light on the further optimization on the fabrication process (Dong et al., 2015; Nie et al., 2015; You et al., 2014a; Zhu et al., 2014). To some extent, the two-step solution deposition (two-step procedure) can bring more uniform, pinhole-free, good

coverage MAPbI₃ films compared to the one-step procedure (Burschka et al., 2013; N.J. Jeon et al., 2014). However, two-step procedure method has rarely been used in PCBM-based inverted planar PVSCs (Heo et al., 2015; Zhu et al., 2014). This is mainly because that MAPbI₃ film formed by two-step procedure is relatively rough, and PCBM hardly fills in the undulations of MAPbI₃ film to attain a good interface for the charge transfer and collection (Dong et al., 2015; Seo et al., 2014; Wang et al., 2014; Wu et al., 2015; Xiao et al., 2014b). Xiao reported an effective solvent annealing of MAPbI₃ formed by two-step procedure (Xiao et al., 2014b). Moreover, light soaking effects (Docampo et al., 2013) and hysteresis behaviors in photovoltaic responses will bring considerable inconvenience on the application (Snaith et al., 2014). Polarization and defects were considered as the origin of light density-voltage (J-V) hysteresis, which often was associated with the contact material (Snaith et al., 2014), perovskite sizes (Kim and Park, 2014; Xiao et al., 2014b), the thickness of mesoscopic and compact layer (Kim and Park, 2014), trapping/de-trapping of charge carriers (Snaith et al., 2014), ion migration (Dualet et al., 2014a), and ferroelectricity (Dualet et al., 2014a; Snaith et al., 2014). Kim reported that the grain size of MAPbI₃ perovskite was associated with the J-V hysteresis directly (Kim and Park, 2014). Xiao reported that the increased grain size of MAPbI₃ could be contributed to the decreased surface traps, and the balanced hole flux and electron flux, which can reduce the hysteresis of PVSCs effectively (Xiao et al., 2014a). When exposed to humidity moisture, PVSCs will decompose quickly due to the highly hygroscopic nature of halide

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perovskite materials (Suarez et al., 2014). In parallel with the work on improving PCE of the PVSCs, less work are involved in the device stability of PVSCs (Mei et al., 2014; You et al., 2016). It is necessary to develop new method to optimize the perovskite active layer, in view of there are limited studies on the stability, light soaking effects and hysteresis behaviors of PCBM-based inverted planar perovskite devices which are fabricated by two-step procedure (Chiang and Wu, 2016; Perumallapelli et al., 2016; Shao et al., 2014; Xiao et al., 2014b; Zhao et al., 2015).

In our work, highly reproducible and photocurrent hysteresis-less inverted planar PVSCs are demonstrated from a modified method with the device structure of ITO/PEDOT:PSS/MAPbI₃/PCBM/Ca/Al. Using the residue solvent N,N-dimethylformamide (DMF) of PbI₂ after spin-coating, the much slower DMF evaporation gave PbI₂ a perfect solvent annealing at a low temperature of 40 °C. Based on the modified solvent annealing method, other fabrication conditions including thickness of the PbI₂ film, concentration and loading time of MAI, annealing temperature and annealing time of MAPbI₃ have been systematically investigated for a further enhancement of device performances.

2. Experimental

2.1. Materials and reagents

Anhydrous N,N-dimethylformamide (DMF, 99.9%), anhydrous, chlorobenzene (CB, 99.9%), methylamine (CH₃NH₂, 33 wt% in MeOH), hydroiodic acid (HI, 57 wt% in H₂O), anhydrous 2-propanol (IPA) and PbI₂ (99.999%) were purchased from commercial suppliers and used as received, PC₆₁BM was obtained from American Dye Source, Inc., poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS) solution (AI4083, Germany) was purchased from Clevios.

CH₃NH₂I (MAI) was synthesized according to the reported method (Lee et al., 2012): 15 mL of methylamine (40% in water, TCI) was added into 16.5 mL of hydroiodic acid (57 wt% in water, JK Chemical) at 0 °C for 2 h with stirring under air. After that the remaining liquid was evaporated in a rotavapor at 50 °C for 2.0 h, and a white colored powder was formed during this process. The white powder was collected and washed with diethyl ether three times, then the as-obtained product was re-dissolved in 40 mL absolute ethanol and precipitated with the addition of 200 mL diethyl ether, this procedure was repeated three times. The solid was collected and dried at 60 °C in vacuum oven for 24 h.

2.2. Fabrication and characterization of perovskite solar cells

The patterned indium tin oxide (ITO) glass (15 Ω □⁻¹) was pre-cleaned in an ultrasonic bath with deionized water, acetone and IPA, finally treated under an ultraviolet-ozone chamber for 10 min. Firstly, PEDOT:PSS was spin-coated on top of ITO glass at 4000 rpm for 30 s, then baked at 150 °C for 10 min and transferred to the glove box. PbI₂ was dissolved in DMF (463 mg mL⁻¹), and MAI was dissolved in IPA (8–40 mg mL⁻¹). The PbI₂ precursors were then spun onto PEDOT:PSS-covered ITO glass at 2000–8000 rpm for 30 s and annealed at 40 (modified method), 50, 60 and 70 °C (control method) for 10 min in N₂, or annealed at 40 and 70 °C by adding DMF at the edge of the petri dish, then MAI/IPA (0.8 mL) was first drop from one corner of the ITO to the top of PbI₂ layer with about 5 s, then spin-coated at 3000 rpm for 30 s after a loading time between 60 and 180 s. The loading time of MAI is the period in which all of the MAI/IPA solution swells on the spin coater. MAPbI₃ were thermally annealed on at 90–100 °C in N₂ or annealed by adding DMF at the edge of the petri dish for 5–120 min. Then PC₆₁BM was deposited by spin-coating

with a concentration of 20 mg mL⁻¹ in CB at 1000 rpm for 45 s and the films were annealed at 90 °C for 5 min. Finally, the devices were transferred to a vacuum chamber and completed with the evaporation of 20 nm Ca and then 100 nm Al electrode through a shadow mask. The cells were encapsulated with glass by UV-curable resin in a glove box then measured in air.

Solar-simulated AM 1.5 sunlight was generated with an ABET class AAB solar simulator calibrated to give 100 mW cm⁻² using an NREL-calibrated KG5-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1.0%. The *J*-*V* curves were recorded with a Keithley 2400. The active area of the solar cells was defined with a metal aperture mask of about 0.04 cm². The external quantum efficiency (EQE) values of the solar cells were measured (Enlitech QE-R3011) at room temperature.

3. Results and discussion

PVSCs were fabricated with the structure of ITO/PEDOT:PSS/MAPbI₃/PC₆₁BM/Ca/Al. Using the two-step procedure of MAPbI₃, the filtered PbI₂ was annealed at 70 °C for 10 min after spin-coating with the control method (Xiao et al., 2014a). The PVSCs were optimized with different PbI₂ spin speed, concentration of MAI, annealing temperature and time (Table S1, ESI†). These devices have noticeable light soaking effects as it is shown in Fig. 1a. PCEs typically increased to 8.0–8.5% after 10–15 min of constant illumination (Fig. 1a). The best device obtained by the control method showed a low PCE of 4.15% with a *V*_{oc} of 0.68 V, a *J*_{sc} of 11.72 mA cm⁻² and a FF of 52.08% on initial light exposure (Fig. 1a, *t* = 0 min) and the enhanced device performances were obtained with a *V*_{oc} of 0.88 V, a *J*_{sc} of 14.42 mA cm⁻², a FF of 67.29% and the resulting PCE of 8.49% after 15 min light soaking (Fig. 1a, *t* = 15 min). Same phenomena of light soaking were reported by other groups (Docampo et al., 2013; Zhao et al., 2015), *J*_{sc}, *V*_{oc} and FF continuously increase with light illumination. Very recently, Nie et al. proposed a mechanism based on the changes in the sub-gap density of states over illumination time in the perovskite active layer (Nie et al., 2016). The long light soaking period of PVSCs to reach the steady-state condition also affects the hysteresis phenomena (Kim and Park, 2014).

In our modified solvent annealing method, PbI₂ was annealed by the residual DMF after spin-coating at 40 °C for 10 min. For a clear comparison, the best fabrication condition for the devices fabricated by the control method is used in the modified solvent annealing method firstly, except the annealing condition of PbI₂ film. No need in additional solvent, the moderate solvent annealing in the evaporation process after spin-coating can promote the self-assembling of PbI₂ within the optimum time for the formation of crystal phase. Device performances were shown in Fig. 1b with a *V*_{oc} of 0.82 V, a *J*_{sc} of 16.63 cm⁻², a FF of 66.30%, and a PCE of 8.99% on initial light exposure, and a *V*_{oc} of 0.86 V, a *J*_{sc} of 16.67 cm⁻², a FF of 64.10%, and a PCE of 9.17% obtained after 15 min of constant illumination. The modified solvent annealing of PbI₂ significantly improved *J*_{sc} and FF of the PVSCs. Interestingly, the resulting devices have not present obviously light soaking effects. It seems that the residual DMF after spin-coating is an appropriate amount for the PbI₂ annealing. The devices also show excellent reproducibility in the different batch experiments. DMF has a low volatility with a higher boiling point (152.8 °C) and lower saturated vapour pressure (3.46 kPa at 60 °C), which can give big freedom of DMF–PbI₂ complexes and will not inhibit crystallization of PbI₂ in a relatively long time at 40 °C. Fast reaction of MAI and PbI₂ upon contact was evidenced by the color change of PbI₂ films immediately from yellow to black brown. Since both PbI₂ and MAI have high solubility in DMF, the DMF–PbI₂ complexes provided a relatively wet reaction environment, so that the MAPbI₃

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